

Organic Photovoltaics Based on Self-Assembled Mesophases

Bernard Kippelen,^{(a)*} Seunghyup Yoo,^(a) Benoit Domercq,^(a)
Carrie L. Donley,^(b) Chet Carter,^(b) Wei Xia,^(b) Britt A. Minch,^(b)

David F. O'Brien,^(b) and Neal R. Armstrong^(b)

^(a)Optical Sciences Center, University of Arizona, Tucson, AZ 85721, USA

^(b)Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA

ABSTRACT

We report on the photovoltaic properties of cells containing new soluble discotic liquid crystalline copper phthalocyanines. Highly ordered structures are obtained by thermal annealing of spin-coated thin films. Bi-layer solar cells using C₆₀ as an electron transport layer were fabricated. The annealing of the phthalocyanine layer resulted in a 3.5 times increase of the short-circuit current density and a reduction of the series resistance. The performance and limitations of photovoltaic cells fabricated from self-assembled organics are discussed.

1. Introduction

Organic molecules and polymers have recently attracted a great amount of interest as semiconducting materials, and have been successfully applied to electroluminescent devices, field-effect transistors, and photovoltaic cells. Because organic materials can be processed at low temperature, they can be fabricated into thin films onto plastic substrates. That property can potentially lead to a new generation of organic solar cells that are light-weight, foldable, flexible and moldable. Furthermore, when roll-to-roll compatible fabrication techniques such as printing are used to process these films from solution, solar cells can potentially be fabricated in large volume at low cost. At this stage, the conversion efficiencies of organic-based solar cells do not compete with those of silicon. Note, that conversion efficiencies of 10% have been demonstrated in dye-sensitized nanocrystalline titanium dioxide films [1]. Unfortunately, the liquid nature of the electrolyte that is used to regenerate the dye limits the long-term stability of such cells as the liquid electrolyte has the tendency to evaporate. Solid state versions of these electrochemical cells have conversion efficiencies of a few percents [2], values that are comparable with those of solid-state organic [3-5] and hybrid organic/inorganic cell geometries [6].

Light absorption in organic materials leads to the creation of excitons that possess a strong binding energy. These excitons can be split into electron-hole pairs when two organic semiconductors with band off-sets larger than the binding energy of the exciton are brought together either by mixing or in a multilayer structure. High photon to current quantum efficiencies can be achieved this way. Although it is a prerequisite for a high photovoltaic energy conversion efficiency, it is only one out of several conditions that need to be met. The challenge is to optimize the product of the photogenerated current and the open-circuit voltage,

while maintaining a large fill factor. The latter is strongly influenced by the values of device parameters such as the series and shunt resistances, the reverse saturation current, and the diode ideality factor. While these parameters could be optimized in silicon-based solar cells, their optimization can be a challenge for organic materials because charge mobility in these nearly amorphous materials is orders of magnitude smaller compared with that of crystalline inorganic semiconductors.

The route we propose to develop highly efficient organic solar cells is to fabricate ordered films from solution with controlled nanophase ordering and high charge mobility by using mesoscopic self-assembly. Through molecular design, new supramolecular building blocks are developed that incorporate the semiconducting functional groups used in amorphous organic solar cells. As a first step in this direction, we have developed and characterized a self-assembled hole transport material that is based on copper phthalocyanine molecules that form discotic liquid crystalline phases.

This report is organized as follows: first we briefly discuss the key properties required to achieve high photovoltaic conversion efficiency and review the current status of organic photovoltaic technologies. Then, we present and discuss the results of various characterization experiments that have been carried-out to get information on the morphology of our self-assembled phthalocyanines. Finally, we discuss their current performance in solar cells.

2. Current Status and Challenges of Organic Photovoltaics

The basic structure of a solar cell consists of two layers of semiconductors that form a p-n junction that are sandwiched between two electrodes, one of which being transparent. For high photovoltaic conversion efficiency the following conditions must be met: (i) the photoactive materials should absorb a broad spectral range of the solar spectrum with a high extinction coefficient; (ii) the exciton diffusion length should be of the order of the thickness of the light absorbing films; (iii) efficient dissociation of excitons into carriers is required over the full spectrum; (iv) materials must have high mobility to reduce series resistance and for efficient charge collection at the electrodes.

In recent years, various schemes for organic photovoltaic devices have been suggested and demonstrated. They can be divided into roughly four categories: (i) dye sensitized electrochemical devices [1-2]; (ii) multilayer devices based on amorphous glasses of small molecules fabricated by vacuum deposition [3-4]; (iii) blends of donor- and acceptor-like conjugated polymers and molecules [5]; and

(iv) hybrid devices consisting of inorganic semiconductor nanostructures blended in a polymer matrix [6].

Because of their amorphous nature, organic semiconductors exhibit short exciton diffusion lengths that limits the thickness of the photovoltaic cells fabricated from these materials. That in return leads to a limited light harvesting. The amorphous structure also limits charge mobility as charge transport occurs through multiple hopping between neighboring molecules or polymer chains. Higher mobility can be obtained in semi-crystalline materials as demonstrated in organic field-effect transistors. In these materials, stacks of molecules are produced and the electronic coupling of adjacent molecules is increased. Such interactions are quantified by the interchain charge transfer integral. Transport in these ordered materials can then be described by band-type theory rather than by inter-site hopping of localized charges, and can lead to higher mobility.

While semi-crystalline films can be obtained by vacuum deposition, it is preferable to develop materials that can be processed from solution. One possible approach to this problem is to develop organic materials that form mesophases such as liquid crystals that self-assemble.

3. Discotic Liquid Crystals for Organic Photovoltaics

Discotic liquid crystals can self-organize to form columnar stacks like in a discotic liquid crystalline phase as shown in Fig. 1a. The intermolecular distance in these highly ordered columnar structures is minimized and lead to strong electronic coupling that is required for efficient charge transport. For instance, mobility values of $0.1 \text{ cm}^2/\text{V s}$ were reported previously in columnar mesophases of discotic liquid crystals [7]. Recently, the liquid crystal hexaphenyl-substituted hexabenzocoronene was combined with a perylene diimide dye in a solar cell configuration. An external quantum efficiency of 34% has been demonstrated at 490nm. However, their photovoltaic performance under standard solar illumination conditions was limited by their small absorption in the red part of the spectrum and by a saturation of the photocurrent at light intensities higher than $1 \text{ mW}/\text{cm}^2$ [8].

4. Experimental Results

For our study, we synthesized the molecule 2,3,9,10,16,17,23,24-octakis(2-benzyloxyethylsulfanyl) phthalocyanato copper(II) (DL-CuPc) shown in Fig. 1b. These molecules exhibit a discotic liquid crystalline phase transition temperature of 134°C , and are soluble in most common organic solvents. Moreover, this molecule has a high extinction coefficient that is similar to that of its parent molecule CuPc that has been used as a hole transport layer in organic small molecule solar cells [3,4].

We fabricated high quality thin films by spin-coating of DL-CuPc. Thermal annealing of these films allows

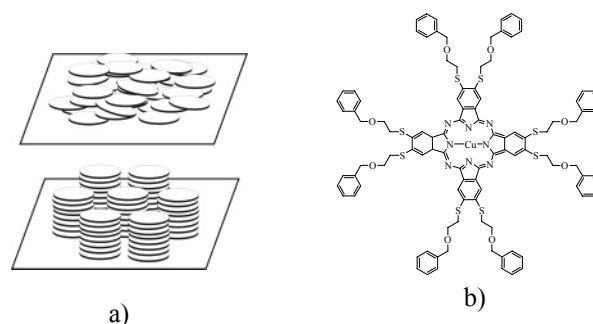


Figure 1. (a) Schematics of a nematic discotic phase and a columnar discotic phase; (b) molecular structure of DL-CuPc.

for the molecules to self-organize into liquid crystalline mesophases. These phases have been characterized by optical spectroscopy, AFM and small angle X-Ray diffraction. To test the photovoltaic properties of these materials, we incorporated them into bilayer devices, in which the electron transport layer was C_{60} . Devices with structure ITO/PEDOT:PSS(30 nm)/DL-CuPc (20 nm)/ C_{60} (40 nm)/BCP (10 nm)/Al in which the hole transport layer was annealed exhibited a short-circuit current density (J_{sc}) and a fill factor (FF) of $0.42 \text{ mA}/\text{cm}^2$, and 0.39, respectively, under white light illumination of $46 \text{ mW}/\text{cm}^2$ from a 150W Xe lamp with AM 1.5 D correction filters. No correction has been made to account for spectral mismatch of the lamp with true AM 1.5 D spectrum. Under the same conditions, a device with a non-annealed hole-transport layer had $J_{\text{sc}} = 0.12 \text{ mA}/\text{cm}^2$ and $\text{FF} = 0.32$ (see Fig. 2). Products of the series resistance and the area of these devices (0.1 cm^2) were estimated by the equivalent circuit model using eq. 1 to be $6.2 \Omega \text{ cm}^2$ (non-annealed), and $1.5 \Omega \text{ cm}^2$ (after annealing), respectively,

$$J = \frac{1}{1 + R_s/R_p} \left[J_0 \left\{ \exp\left(\frac{V - J R_s A}{nkT/e}\right) - 1 \right\} - \left(J_{\text{ph}} - \frac{V}{R_p A} \right) \right] \quad (1)$$

Reduction in the series resistance of devices with annealed films can be attributed to an increase in charge mobility associated with a high degree of ordering of the DL-CuPc molecules following the annealing process.

5. Discussion

Small-angle X-ray diffraction results shown in Fig. 3 support the increased ordering of spin-coated film upon annealing. However, the data suggest that the molecules are lying down on the substrate rather than forming vertical stacks that are perpendicular to the surface. The three diffractions peaks shown in Fig. 3 suggest that the molecules self-assemble into at least three different packing geometries. Figure 4 shows the absorption spectra of the molecule in solution and as a solid film spin-coated from chloroform. The absorption spectrum of films shows multiple peaks, with both red-shifted and blue-shifted maxima, suggestive of at least three different phases, with different degrees of ‘stagger’ between phthalocyanine rings (J-aggregate-like vs. H-aggregate-like staggering).

AFM images (see Fig. 5) show that thermal annealing results in ‘rough’ surfaces with micron- to sub-micron size features. This texturing can explain the increase in short-circuit current density that was observed in cells fabricated from these materials. However, this also caused increase in leakage paths, resulting in reduction of the open-circuit voltage. With proper control of the size and depth of these pores, this effect may be very useful in creating ‘inter-penetrated’ networks where efficient separation of excitons is promoted while good transport paths are still preserved.

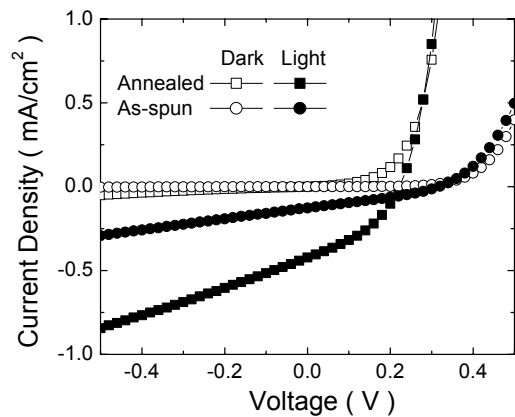


Figure 2. Electrical characteristics of annealed and as-spun devices with structure ITO/PEDOT:PSS (30nm)/DL-CuPc (20nm)/C₆₀ (40nm)/BCP (10nm)/Al, under 46 mW/cm² (150W Xe lamp with AM 1.5 D filters)

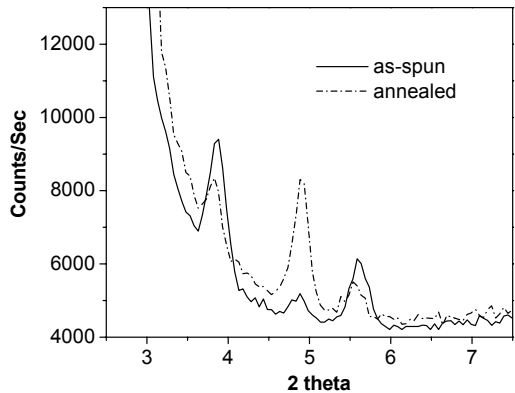


Figure 3. X-ray diffraction measured from a DL-CuPc film on ITO before and after annealing.

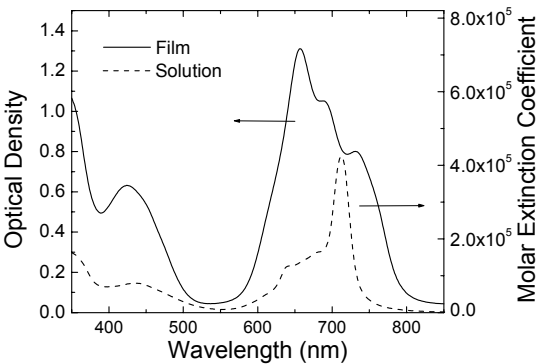


Figure 4. UV/VIS Absorption Spectra of DL-CuPc : spin-coated film (30 mg/ml, 500 rpm) and of solution (6.3x10⁻⁶ M) in chloroform.

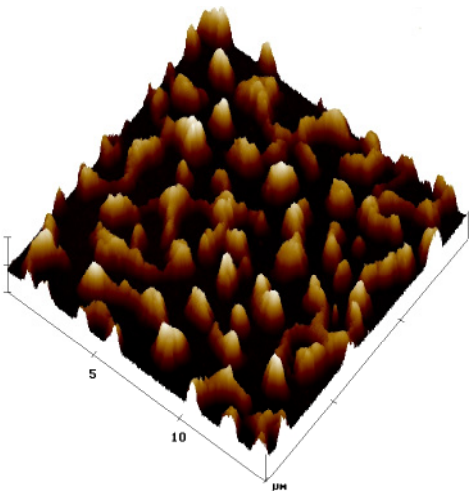


Figure 5. AFM image of annealed DL-CuPc film (spun at 4000 rpm, from 8 mg/ml solution) on PEDOT:PSS/ITO. 5um/div in X, Y axes, and 150 nm/div in Z axis.

6. Conclusion

We demonstrated that DL-CuPc can be a good candidate for hole transporting medium in organic photovoltaic cells. It is soluble in common organic solvents, and has relatively higher absorption in the red (600-800nm). When combined with an electron transport material absorbing in the green and the blue such as C₆₀ or perylene derivatives, photovoltaic cells with broad harvesting of the solar spectrum can be achieved. Moreover, thermal annealing of DL-CuPc at temperature within discotic mesophases can allow molecules to self-organize into columnar stacks to improve transport properties. In addition, we showed that nanostructured surfaces can be generated by thermal annealing, and this may be utilized for creation of interpenetrated networks which are good for efficient carrier generation.

ACKNOWLEDGEMENTS

This work was partially supported by DOE, NSF through a CAREER grant, the Office of Naval Research, and by the State of Arizona through Proposition 301 Initiative.

REFERENCES

- [1] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, "Conversion of light to electricity by cis-X₂Bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X = Cl⁻, Br⁻, I⁻, CN⁻, and SCN⁻) on nanocrystalline TiO₂ electrodes", *J. Am. Chem. Soc.* **115** (1993), pp. 6382-6390.
- [2] U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Speitzer, M. Grätzel, "Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies", *Nature* **395** (1998), pp. 583-585.
- [3] C. W. Tang, "Two-layer organic photovoltaic cell", *Appl. Phys. Lett.* **48** (1986), pp. 183-185
- [4] P. Peumans and S. R. Forrest, "Very-high-efficiency double-heterostructure copper phthalocyanine/C60 photovoltaic cells", *Appl. Phys. Lett.* **79** (2001), pp. 126-128.
- [5] S.E. Shaheen, C.J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen, "2.5% efficient organic plastic solar cells", *Appl. Phys. Lett.* **78** (2001), pp. 841-843.
- [6] W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos, "Hybrid nanorod-polymer solar cells", *Science* **295** (2002), pp. 2425-2427.
- [7] D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, and D. Haarer, "Fast photoconduction in the highly ordered columnar phase of a discotic liquid crystal", *Nature* **371** (1994), pp. 141-143.
- [8] L.Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, and J. D. MacKenzie, "Self-Organized Discotic Liquid Crystals for High-Efficiency Organic Photovoltaics", *Science* **293** (2001), pp. 1119-1122.